SYNTHESIS, CHARACTERIZATION AND CATALYTIC APPLICATION OF LAYERED DOUBLE HYDROXIDES BASED MATERIAL

SYNOPSIS

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Introduction

In today's world of research and technology, material science is essentially utilized in various types of manufacturing, housing, agriculture, transportation, and other applications to satisfy the needs of individuals. The rapid advancement in different properties of solids has created a variety of new options for better understanding and application of various materials (Kakani, 2004). The different types of materials have been studied and are usually divided into four categories: metals, polymers, semiconductors, and ceramics. Ceramics have attractive properties and advantages over metals and polymers, like high-temperature strength, superior wear resistance, high hardness, reduced thermal and electrical conductivity, and chemical stability. These are better suitable for specific applications such as aerospace, energy, and optics due to their unique characteristics (Samant & Dahotre 2009; Zhang et al., 2020). Clays are belonging to ceramic materials and are utilized as excellent adsorbent materials for gases and removal of hazardous metal ions from aqueous solutions. Clays have several advantages over many other commercially available adsorbents, including low cost, abundant availability, high specific surface area, excellent adsorption properties, non-toxicity, and a large potential for ion exchange (Uddin, 2017). Clay materials have attracted the intention of scientists and researchers because of their unique features and low cost of production. Clays are also used as potential material for various applications such as sensors, mineralization, and catalysis (Srinivasan, 2011). These materials have a wide range of uses due to their distinctive features, which include high specific surface area, structural features, and chemical and mechanical stabilities (Adeyemo, Adeoye & Bello, 2017). There are two types of clays.

Cationic or Smectite Type

These clays feature a layered lattice structure in which layers of hydrated cations separate two-dimensional oxyanions (Greenwell et al., 2006). Cationic clays are mostly made from natural materials that invariably contain impurities such as quartz, calcite, feldspars, and other minerals, but they can also be made synthetically. Commercially modified montmorillonites, such as K10 or KSF, are commonly utilized as acid catalysts or adsorbents in the hydrocarbon cracking and petroleum industry. The acronyms "Clayfen" and "Claycop" stand for iron (III) or copper (II) nitrate supported on K10 clay, respectively (Vaccari, 1998).

Anionic or Brucite type

These clays have a positive charge on the metal layers and compensate for anion in interlayer space/gallery (Greenwell et al., 2006). Anionic clays are frequently utilized as adsorbents, ion exchangers, and catalytic material in industry and laboratories to produce regio- and stereo-selective products. Chemical composition, basal spacing, and stacking sequence are characteristics of these types of clays. Hydrotalcites are natural or synthetic lamellar mixed hydroxides with interlayer spaces containing exchangeable anions that are given different names depending on the composition and polytype form (Vaccari, 1998). In recent years, hydrotalcite-like anionic clays have gained spectacular success in heterogeneous catalytic processes, pollutant adsorption, photocatalytic materials, etc. (Sangeetha, 2007).

Hydrotalcite-like anionic clays (HTs) also referred to as layered double hydroxides (LDHs) have a two-dimensional structure. These materials are similar to the minerals like hydrotalcite and marcasite that are found in nature (Rojas, 2012; Yang et al., 2015). HTs/LDHs have the general formula $[(M^{2+})_{1-x}(M^{3+})_x(OH)_2]^{x+}(A^{m-}_{x/m}).nH_2O$ where M^{2+} and M^{3+} are divalent and trivalent cations, respectively, while A^{m-} is the charge balancing anion in the interlayer space (Richardson, 2013). In these compounds, divalent cations within brucite-like layers are replaced by trivalent cations. Hydrated anions are present in the interlayer space between two brucite sheets of metal cations and compensate positive charge of metal layers (Kwon, Tsigdinos & Pinnayaia, 1988; Kumari et al., 2022). Through the calcination or microwave treatment, HTs/LDHs could be utilized as a precursor for the synthesis of mixed metal oxides (MMOs) (Zhao et al., 2016; Kumari et al., 2022; Wu et al., 2013; Klemkaite et al., 2011).

Mixed metal oxides contain two or more different types of metal cations and are generally termed binary and ternary (Gawande et al., 2011). The presence of two or more metals in an oxide matrix results in the varied physical and chemical properties that improve performance in several technological applications (Juma et al., 2017; Gawande, Pandey & Jayaram 2012). The physical and chemical properties have been altered due to the metal-metal (M-M) or metal-oxygen-metal (M-O-M) interactions (Rodriguez et al., 2003; Liu et al., 2011). The M-M or M-O-M interactions in MMOs can result in the change of electronic states that are not seen in single-metal oxides (Rodriguez, 2002). The electrical, optical, catalytic, and chemical properties of MMOs have received a lot of attention in recent years from both scientific and technological perspectives (Paul & Neogi, 2019; Fernandez-Garcia et al., 2002).

Bimetallic catalysts have proven useful for studying the link between catalytic activity and catalyst particle structure (Toshima & Yonezawa, 1998). Layered double hydroxide-based catalytic materials provide various advantages over the corrosive catalysts in the context of green chemistry, which include recycling, simple separation from the reaction mixture, and high surface area that boosts their catalytic activity. They received a lot of interest from chemists for their usage in the field of organic synthesis due to the relationship of the numerous primacy factors with HTs.

Literature review

Layered double hydroxide-based catalytic materials have been used as innovative research materials for a long time. Many studies have reported the preparation and use of layered double hydroxide-based catalytic materials.

Liu et al. (1996) have reported the use of $La_{2-x}Sr_xCuO_{4\pm\lambda}$ (λ nonstoichiometric oxygen) mixed metal oxides for phenol hydroxylation. The XRD and IR spectra show that catalysts remain unchanged after reaction and remain active up to 10 cycles.

Wang & Weng (1997) have reported the use of mixed metal oxide for destructive oxidation of $(CH_3)_2S_2$. $CuO\text{-}MoO_3/\text{-}Al_2O_3$ catalyst showed higher activity and better resistance to deactivation by sulfur compounds.

Goldwasser et al. (2005) disclosed the catalytic performance of mixed-oxide $LaFe_{1-x}Co_xO_3$ for the formation of syngas by methane reforming with CO_2 and O_2 and evaluated the effect of Fe-Co interaction on methane reforming.

Jongsomjit, Ngamposri & Praserthdam (2005) have revealed the use of TiO_2/SiO_2 supported methylaluminoxane with rac-$Et[Ind]_2ZrCl_2$ (toluene, rac-ethylene bis (indenyl) zirconium dichloride) catalyst for the synthesis of linear low-density polyethylene.

Perez-Alonso et al. (2006) have reported the utilization of mixed metal oxides $Fe_xCe_{1-x}O_2$ for N_2O decomposition with greater reaction stability at high temperatures.

Lucarelli et al. (2007) have prepared the binary and ternary mixed oxide of V, Nb, Mo, and Sb by using the sol-gel method and evaluated their catalytic activity for the selective oxidation of propane.

Blanco, Carrazan & Rives (2008) have prepared the MgVAl mixed metal oxides by thermal decomposition method and studied their activity for oxidative dehydrogenation of propane.

Coleman et al. (2009) have reported the use of Ni/Mg-Al mixed metal oxide catalyst for the steam reformation of ethanol and showed the highest conversion into H_2 and CO_x products.

Ma et al. (2010) study, of mesoporous Co_3O_4 and Au/Co_3O_4 low-temperature catalysts with good catalytic activity for trace ethylene oxidation at 0 °C are reported.

Gawande et al. (2011) prepared $MgO\text{-}ZrO_2$ catalyst by ultra-dilution method and investigated catalytic activity in different chemical reactions like cross-aldol condensation, Cbz-protection of amines, catalytic transfer hydrogenation of nitro compounds, and the production of 1,5-benzodiazepine.

Fan et al. (2011) have reported the photocatalytic activity of ZnAlIn-MMO due to the larger specific surface areas with band gaps of 2.50-2.60 eV.

Li et al. (2011) have reported the preparation of Sn-Cu mixed metal oxide nanowire through thermally oxidizing electrodeposition technique and further investigate the sensing capabilities against the volatile compounds.

Gawande et al. (2012) have summarized the catalytic properties of different mixed metal oxides in various types of chemical reactions such as reductions, oxidation, and one-pot Mannich reactions.

Verma et al. (2013) prepared the zirconium metal oxides (ZrO_2, $ZrTiO_4$, and ZrV_2O_7) by microwave-assisted citrate sol-gel and solution combustion method and further investigate structural characteristics by using XRD and TEM techniques.

Lan et al. (2013) have studied the photocatalytic degradation of methylene blue dye by using ZnAlIn-MMO nanoparticles.

Yang et al. (2013) prepared graphene oxide/NiAl-mixed metal oxides (rGO/Ni/MMO) by the calcination of reduced graphene oxide -LDH and evaluated the adsorption ability toward methyl orange (MO) in an aqueous solution.

Siriwardane et al. (2013) prepared the Cu-Fe mixed metal oxide by the solid-state mixing method and further evaluated their oxygen carrier capability.

Lee et al. (2013) have synthesized mixed metal oxide of Mg-Zn by coprecipitation method and used it as a solid base catalyst for the transesterification of non-edible Jatropha oil with methanol.

Orbaek et al. (2015) have investigated the preparation of different Fe-MO nanoparticles and checked the ability to maintain the particle size and shape by the wide composition change of metal atom (M = Fe, Mn, Pd, Cu, Al, Gd).

Tuncelli Ay & Zumreoglu-Karan (2015) have synthesized nitrate precursors of iron LDH with good drug-carrying capacities (Camptothecin drug).

Wang et al. (2015) investigated the antibacterial properties of Mg-Al mixed metal oxide against *Escherichia coli*, *Staphylococcus aureus*, *Pseudomonas aeruginosa*, and *Vibrio fischeri*.

Rasouli, Movahedi & Doudi (2017) disclosed the antibacterial activity of ZnO/MAl_2O_4 (M= Cu, Ni, Mg, and Co) mixed metal oxide against *E. coli* and *S. aureus* bacteria.

Guan et al. (2017) have revealed the excellent electrochemical application of Ni-Co oxides such as high specific capacitance (≈1900 Fg^{-1} at $2Ag^{-1}$), good rate capability, and ultrahigh cycling stability (93.6% retention over 20 000 cycles).

Elhalil et al. (2017) have evaluated the adsorption capacity and photodegradation activity of $ZnO\text{-}ZnAl_2O_4$ mixed oxides with the highest caffeine elimination efficiency (97.32%).

Sultana et al. (2017) have prepared cerium doped nickel-manganese mixed metal oxide and evaluated the catalytic activity of MMO as a catalyst.

Amor et al. (2018) have reported the photocatalytic performance of ZnAlTi nanoparticles for methylene blue degradation and evaluated that by increasing the value of catalyst degradation also increased.

Wang et al. (2020) have studied the bifunctional Co-V MMO nanowire as intrinsic oxidase and peroxidase-like catalytic activities for antibacterial application.

Zhu et al. (2020) have reported the CO_2 uptake from the air by using the $Mg\text{-}Al\text{-}CO_3$ MMO and also evaluated the high stability of catalyst over 20 cycles at 25 °C under 0.4 mbar CO_2.

Batistella et al. (2011) have prepared Mg-Al oxide by co-precipitation method and evaluated the adsorption capacity of fluorine ions (303.54 $mg.g^{-1}$) to remediate fluorine-contaminated water.

Gao et al. (2013) investigated the CO_2 adsorption characteristics of $Mg\text{-}Al\text{-}CO_3$ mixed metal oxides and also evaluated the high-temperature CO_2 adsorption ability of this material.

Koilraj et al. (2013) evaluated the phosphate treatment by using NiAl LDHs and used as fertilizer for the growth of seaweed Ulva Lactuca.

Li et al. (2019) have incorporated the Penicillin G into ZnAl-LDH by co-precipitation method and evaluated the antibacterial testing against *Escherichia coli.*

Zhang et al. (2019) have prepared ZnZrAl metal oxide and evaluated catalytic performance for ethanol conversion to synthesize DEC (diethyl carbonate).

Abd Elhaleem et al. (2020) have investigated the use of Zn-Al LDH/cefotax against second-degree burn wound infection. LDH and PVA nanofibers have good cefotax carrier ability with control release of cefotax for a long time.

Hanif et al. (2021) have prepared Mg-Al MMOs by co-precipitation method and used them for NO_2 removal as the adsorbents.

Research gap identification

Even though a huge number of research groups from around the world created the mixed metal oxide and studied its properties, many fields have to be found. Also, mixed metal oxide has some interesting properties different from the conventional metallic catalyst, which attracted the focus of this research in this area. In addition, this application of synthesized mixed metal oxide for catalysis needs much more attention.

Proposed objectives

The following objective is designed to fulfill the aim.

- Synthesis of layered double hydroxide-based catalytic materials.
- Characterization of the synthesized layered double hydroxide-based catalytic materials by various characterization techniques like XRD, FTIR, SEM-EDS or EDX.
- Evaluation of catalytic applications of layered double hydroxide-based material.

Proposed Methodology

In the literature, different methods are reported for the synthesis of mixed metal oxide nanoparticles. In our study, we use the co-precipitation method.

Method

For the preparation of mixed metal oxide nanoparticles, a fixed amount of divalent and trivalent salts will be mixed with a fixed volume of NaOH and Na_2CO_3 solution until the pH will be adjusted to a particular range. At this pH, a slurry containing crystalline particles will be detected, which will be further stirred under heating. After cooling the slurry, the precipitate will be filtered followed by washing with deionized water. The obtained hydrated complex will be dried in an oven at 110 ºC and calcined at 500 ºC for 5 hours to obtain mixed metal oxide powder.

Thesis Outline:

Chapter 1 (Introduction): The chapter will include the introduction of metal oxide and mixed metal oxide particles. The chapter will also include the application activities.

Chapter 2 (Literature Review): This chapter includes the various hypothesis and research of different authors. This chapter also includes the research gap identified.

Chapter 3 (Materials and Methods): This chapter contains information about the experiment and the instruments used. This chapter also provides the research approaches and steps.

Chapter 4 (Results and Discussion): This chapter deals with the results/outcomes of the prepared mixed metal oxide. It also includes the results of different characterization techniques and catalytic applications.

Chapter 5 (Summary and Conclusion): This chapter will include a summary of the entire study based on the objectives, as well as findings. This chapter also includes the future scope of the research.

Chapter 6 (References): This chapter includes the references to books, reports, and research papers of the authors associated with the ongoing research.

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CERTIFICATE
(SYNOPSIS APPROVAL CERTIFICATE)

This is to certify that the Synopsis for Ph.D. Thesis titled, **"SYNTHESIS, CHARACTERIZATION AND CATALYTIC APPLICATION OF LAYERED DOUBLE HYDROXIDE BASED MATERIAL"**, submitted by **Ms. Savita Soni** to the Career Point University, Hamirpur (H.P.), India in partial fulfillment of the requirements for the degree of **DOCTOR OF PHILOSOPHY** in the Department of **Chemistry**, School of **Basic and Applied Sciences** has been approved by the Research Advisory Committee (RAC) after an Oral Examination of the student on dated 28.06.2022.

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